

STORMWATER MONITORING IN 1999 AND 2000 AT NOLAND DIVIDE AND LECONTE CREEK IN THE GREAT SMOKY MOUNTAINS NATIONAL

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INTRODUCTION

The Great Smoky Mountains National Park (GRSM) is the largest temperate-zone national park in the eastern United States, and offers one of the most biodiverse ecosystems in the U.S. The GRSM also has within it five streams designated as Outstanding National Resource Waters (ONRW). These streams and others within the Park are threatened with impairment by the highest acid deposition rate received by any park. The high acid deposition is already suspected to have caused trout loss in multiple stream reaches.

The present understanding of water chemistry in streams of the GRSM is largely based upon periodic sampling efforts. Although the GRSM has a water quality monitoring program that collects stream samples throughout the Park, the monitoring is focused on baseline conditions through quarterly grab samples that, by their nature, are hydrologically biased against storm or episodic events. Baseline sampling is very important for understanding average (chronic) water quality conditions and for monitoring long-term trends. But baseline monitoring fails to characterize the worst water quality (acute) conditions, and does not reflect the most extreme stresses on aquatic life that occur during storms.

Biologists indicate that recent fish surveys have shown declining populations of some pollution-sensitive species in many headwater streams in the Park. Fisheries biologists and anglers are especially concerned about a decline in brook trout populations, which is the only salmonid species native to the Park. For example, the unexplained distribution of trout populations in some streams in the Park is an important issue for NPS fishery biologists, and may be related to natural habitat characteristics or differences in water quality that could be associated with episodic water-quality conditions. The effects of transient water-quality conditions prevailing during storm events, especially high concentration of dissolved metals, have not been extensively investigated, but might help explain observed biological distributions. Pulses of elevated concentrations of certain chemical constituents associated with storm events could have a cumulative effect on the freshwater fauna and pose a threat to aquatic organisms.

The occurrence of acidic atmospheric deposition in the Park may be contributing to the mobilization of some metals such as aluminum and the depletion of major cations that can alter the ion exchange reactions in soil. Significant decreases in pH and alkalinity combined with increased nitrate concentrations and conductivity have been observed during heavy storm events for some streams in the Park. The few storm event studies performed in the GRSM have shown pH drops from 6.5 to an average of 5.0 over a two-day episodic event with pH excursions down to 4.6. In addition, storm event studies have shown increases in nitrate indicative of incipient N-saturation which is associated with acidification and has broad consequences for ecosystem disruption. Aluminum hydroxide precipitate has been observed within the Park (Beech Flats Creek) and could be redissolved with downward fluctuations in pH possible during storm events. Storm event studies have also shown five-fold and more increases in aluminum to well above toxic thresholds.

As part of the National Park Service (NPS)-U.S. Geological Survey (USGS) Water Quality Assessment and Monitoring Partnership, the USGS provided technical assistance to the NPS on designing and initiating a storm-event sampling program. This work began in FY99 with the installation of automated water samplers and stream gauges at two sites on LeConte Creek and two sites in the Noland Divide Watershed (NDW). The knowledge gained from this investigation provides valuable insight, and serves as a guide for the design and implementation of future research with a stormwater sampling component.

Purpose and Scope

This report briefly describes the efforts of the NPS (in cooperation with the University of Tennessee (UT) and with USGS technical assistance) to implement storm-event sampling to supplement their ongoing water-quality sampling program. The report describes the cooperative effort between the agencies that conducted the investigation, and presents results of sample analyses for samples collected in LeConte Creek and the NDW during several storm events that occurred in 1999 and 2000.

Originally, project plans were to establish three monitoring stations at sites along a longitudinal axis of Noland Creek, of which two sites were extremely remote. GRSM researchers reevaluated the original proposal and suggested an alternate plan that was considered more feasible and beneficial to the Park in terms of addressing the more relevant water-resource management issues.

METHODOLOGY

Site Descriptions

There were four locations where storm-event sampling occurred. Two high elevation monitoring stations were located within the NDW, and two mid-elevation monitoring stations were located on LeConte Creek. Since 1991, the NDW monitoring stations have been monitored by weekly grab samples from two streams (i.e., the southwest and the northeast streamlets, which together form Noland Creek) draining the watershed. The two streamlets are located within the spruce-fir forest at 5,840 feet in elevation. The NDW receives atmospheric inputs of sulfur and nitrogen at rates as high as any forested ecosystem in North America, and is subject to the same environmental pressures as many of the other high-elevation watersheds in the Park. The LeConte mid-elevation monitoring stations were originally part of the Park-wide intensive monitoring program from 1993-1995. These monitoring stations are located within the Cove-Hardwood forest. Lower LeConte Creek (LLC) monitoring site was located near Twin Creeks Research Station at an elevation of 1,940 feet. The Upper LeConte Creek (ULC) monitoring site

was located approximately 2.5 miles upstream at an elevation of 2,880 feet. The absence of trout above elevation 2883 feet on LeConte Creek is an important issue but its cause is unknown

Equipment Descriptions

Four ISCO automated samplers were installed at the sampling sites. The samplers were controlled by dataloggers that were programmed to collect samples at specified volumes and sampling intervals. The samplers were powered with a 12-volt marine battery equipped with recharging solar panels. The samplers were designed to use a liquid level actuator that would trigger the unit to begin sampling whenever the water level rose to a predetermined gauge height. However, the ionic strength of the stream water was too low to activate the water level sensors; therefore, the USGS devised a system that used a float and micro-switch to trigger the sampler. The float/micro-switch system was successful, however the performance of this system also proved problematic.

Streamflow monitoring equipment (pressure transducers and staff plate gauges) was installed at the LeConte Creek sites to record stream stage (streamflow at the NDW sites already was being monitored). The samplers and pressure transducer cables were housed in a gauge shelter to protect the instrumentation from wildlife and possible damage.

Field and Laboratory Procedures

At least four storms per year were planned to be monitored and sampled at each site. Although this objective was achieved, the summer drought conditions created problems that will be discussed later. The auto-samplers were triggered to begin sampling at a preset stage level and then continued to take samples at a preset time interval until all the sample bottles were filled. It was desired to capture the rising limb and peak of the hydrograph but this was problematic because of the limitations of the equipment (as discussed above) and varying durations and intensity of the storms. Park personnel at the Twin Creeks Research Station assisted by observing the sampler at the lower LeConte Creek site to determine if the sampler had triggered and communicated that information to USGS and/or UT personnel so that samples could be retrieved for timely lab analysis. Because of the remoteness of the NDW sites, site visits were required to determine if samplers had triggered, which resulted in a few unproductive site visits. Samples were retrieved as soon as possible following sampling of the storm event. Hydrographs or stage records were analyzed to determine which samples represented the desired portion of the stream hydrograph. These selected stormflow samples were then placed on ice and delivered to the laboratory at the University of Tennessee or the USGS field office in Knoxville.

LeConte Creek samples were analyzed for pH and conductivity. For selected storm events, the first sample and the sample with the lowest pH were targeted for further analyses. The first sample was chosen to best represent the first flush of storm water. These samples were analyzed for acid neutralizing capacity and major ions: calcium, magnesium, sodium, potassium, ammonium, sulfate, chloride and nitrate. The analyses were performed at the laboratories of the

Department of Civil and Environmental Engineering at the University of Tennessee, Knoxville using protocols and methods established for water quality monitoring in the Park.

Noland Divide samples from two storm events (total of 21 samples) were measured at the Knoxville field office laboratory for pH and specific conductance, and then shipped on ice to the USGS National Water Quality Laboratory (NWQL) for analysis of inorganic constituents and selected metals. Prior to shipping, samples were filtered through a 0.45 micron capsule filter and treated with the appropriate preservative to stabilize constituents (as required by the NWQL analysis procedures). Chemical analyses conducted by the NWQL included ammonia, nitrate plus nitrite, nitrite, total Kjeldahl nitrogen, total phosphorous, orthophosphate, calcium, magnesium, sodium, potassium, sulfate, chloride, fluoride, silica, filtered (dissolved) and unfiltered (total recoverable) aluminum.

RESULTS AND DISCUSSION

LeConte Creek

At the LeConte sites, the storms on the dates listed in Table 1 below were sampled.

Table 1. Dates of storm events sampled at LeConte Creek

Date of storm sampled	Site	Number of samples
6/25/99	Lower LeConte Creek	24
9/30/99	Upper LeConte Creek	24
10/10/99	Lower LeConte Creek	24
11/2/99	Upper LeConte Creek	24
11/2/99	Lower LeConte Creek	24
6/22/00	Lower LeConte Creek	24
6/22/00	Upper LeConte Creek	24
9/23/00	Upper LeConte Creek	19
9/25/00	Lower LeConte Creek	24
9/26/00	Upper LeConte Creek	25
9/26/00	Lower LeConte Creek	15
10/16/00	Upper LeConte Creek	23

Table 2 summarizes the storm event data and Figures 1 and 2 show a typical storm event. The table shows that the minimum pH observed was 4.36 and occurred at the upper Le Conte Creek site in the June 22, 2000 storm event. The lowest observed pH at the lower site was 4.75 and occurred in the same storm. The minimum pH at the upper site was 0.4 to 0.7 pH units less than at the lower site. The average median pH value at the upper site was 0.25 pH units lower than the lower site. The lower median and minimum pH at the upper site is consistent with the strong pH elevation gradients observed throughout the Park in baseline conditions, i.e., higher elevations

have lower pH. The low pH levels observed would prohibit trout populations if they persisted for sufficient time. Unfortunately, the dose response relationship is poorly defined and influenced by many factors. However, this exploratory storm event research demonstrates the extremes in pH that occur in storm events and the need for increased monitoring and attention to storm events.

Table 2. Summary of LeConte Creek storm event data.

Date ¹	Site ²	Parameter ³	Maximum	Minimum	Median	Mean	Standard Deviation
6/25/1999	LLC	Stage, ft	1.85	1.41	1.73	1.71	0.11
		Cond., $\mu\text{S/cm}$	NA	NA	NA	NA	NA
		pH	NA	NA	NA	NA	NA
9/30/1999	ULC	Stage, ft	1.82	0.95	1.06	1.28	0.37
		Cond., $\mu\text{S/cm}$	41.00	21.80	24.20	27.64	6.24
		pH	6.67	5.90	6.09	6.12	0.15
10/10/1999	LLC	Stage, ft	NA	NA	NA	NA	NA
		Cond., $\mu\text{S/cm}$	18.27	13.00	16.39	16.19	1.28
		pH	6.00	5.74	5.90	5.90	0.08
11/2/1999	ULC	Stage, ft	NA	NA	NA	NA	NA
		Cond., $\mu\text{S/cm}$	24.20	19.77	21.10	21.40	1.30
		pH	5.48	5.08	5.18	5.18	0.08
11/2/1999	LLC	Stage, ft	NA	NA	NA	NA	NA
		Cond., $\mu\text{S/cm}$	22.00	18.30	19.95	20.06	1.02
		pH	6.06	5.77	6.01	5.97	0.10
6/22/2000	ULC	Stage, ft	2.54	1.53	2.32	2.28	0.21
		Cond., $\mu\text{S/cm}$	17.80	15.60	16.45	16.49	0.47
		pH	5.11	4.36	4.63	4.64	0.16
6/22/2000	LLC	Stage, ft	2.02	1.65	1.89	1.90	0.09
		Cond., $\mu\text{S/cm}$	16.00	12.80	14.95	14.82	0.85
		pH	5.14	4.75	5.04	5.01	0.10
9/23/2000	ULC	Stage, ft	NA	NA	NA	NA	NA
		Cond., $\mu\text{S/cm}$	15.90	14.40	15.10	15.23	0.41
		pH	5.65	5.35	5.48	5.50	0.09
9/25/2000	LLC	Stage, ft	NA	NA	NA	NA	NA
		Cond., $\mu\text{S/cm}$	17.90	14.40	16.60	16.55	0.73
		pH	5.80	5.46	5.69	5.69	0.08
9/26/2000	ULC	Stage, ft	NA	NA	NA	NA	NA
		Cond., $\mu\text{S/cm}$	20.70	14.60	15.80	16.10	1.42
		pH	5.21	5.00	5.09	5.10	0.07
9/26/2000	LLC	Stage, ft	NA	NA	NA	NA	NA
		Cond., $\mu\text{S/cm}$	15.10	14.10	14.50	14.60	0.25
		pH	5.81	5.64	5.71	5.71	0.06
10/16/2000	LLC	Stage, ft	NA	NA	NA	NA	NA
		Cond., $\mu\text{S/cm}$	17.77	14.08	14.58	14.80	0.74

	pH	5.78	5.36	5.63	5.60	0.10
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¹The starting date of the multi-day storms is reported

²LLC = lower LeConte Creek, ULC = upper LeConte Creek

³Cond. = conductivity

Figure 1. Storm event at upper site on Le Conte Creek on June 22, 2000.

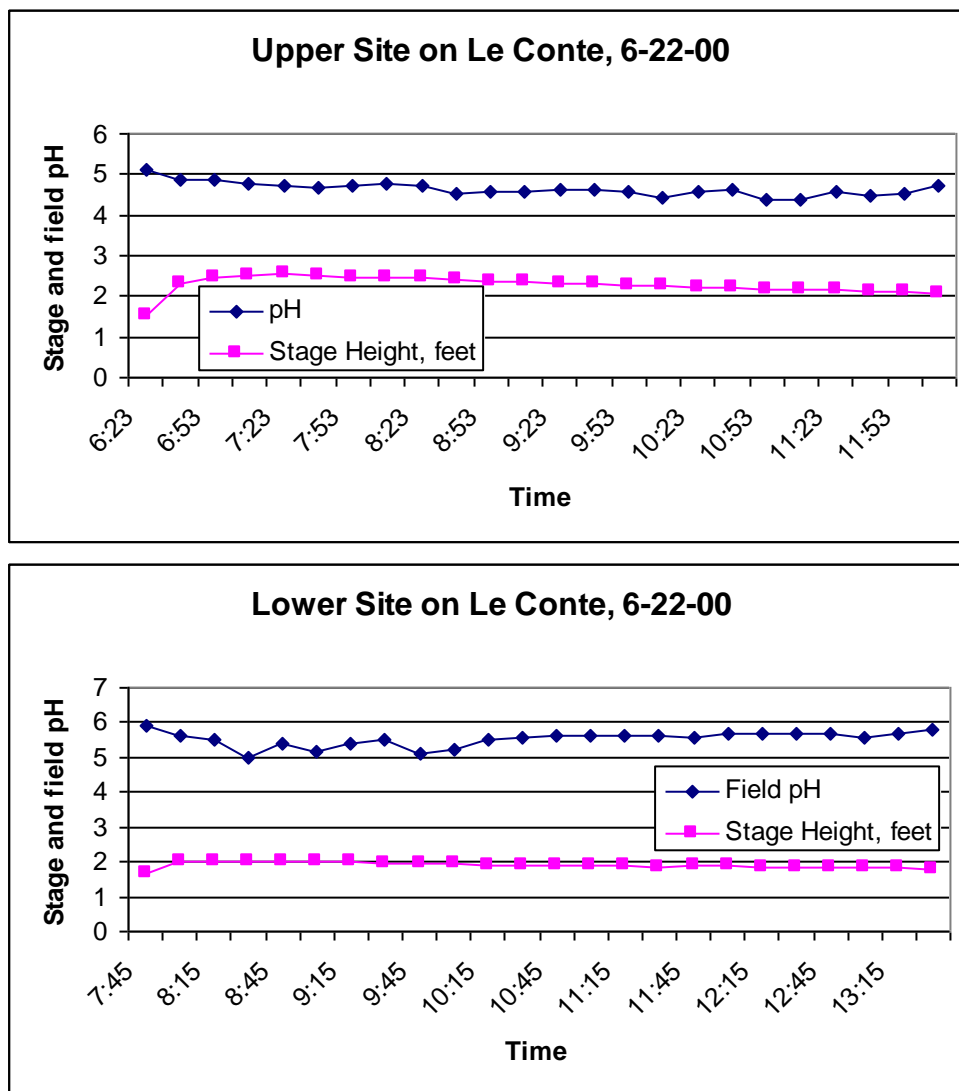


Figure 2. Storm event at lower site on Le Conte Creek on June 22, 2000

Tables 3 and 4 show results of analyses of storm and baseline samples for major ions and acid neutralizing capacity (ANC). Table 5 shows the differences between storm event samples and the 1999 base flow samples and the values reported in a 1997 report summarizing base condition sampling to date. (Sampling of Le Conte Creek was discontinued soon after.) Table 5 indicates significant changes in water quality during a storm. The results show a pH decline of 0.06-0.22 units at the upper Le Conte Creek site and a decline of 0.61-0.80 at the lower site. ANC shows a drop of 3.52-18.85 $\mu\text{eq/L}$ at the upper site and 29.34-34.61 $\mu\text{eq/L}$ at the lower site and essentially eliminates any acid neutralizing capacity in the stream. Interestingly, the lower site shows a greater change in the analytes than the upper site. This was not expected. It was expected that the larger drainage basin at the lower site would attenuate any changes.

Table 3. LeConte Creek storm event sample analyses.

Sample ID	Sample Date or statistic	pH	Cond., $\mu\text{S}/\text{cm}$	ANC	Cl^- , $\mu\text{eq}/\text{L}$	NO_3^- , $\mu\text{eq}/\text{L}$	SO_4^{2-} , $\mu\text{eq}/\text{L}$	Na^+ , $\mu\text{eq}/\text{L}$	NH_4^+ , $\mu\text{eq}/\text{L}$	K^+ , $\mu\text{eq}/\text{L}$	IC Mg^{2+} , $\mu\text{eq}/\text{L}$	IC Ca^{2+} , $\mu\text{eq}/\text{L}$	H^+ , $\mu\text{eq}/\text{L}$
Storm sampling results													
LLC #1	10/10/1999	5.79	15.45	2.20	22.66	40.39	39.89	56.59	0.00	12.16	33.57	72.15	1.62
LLC #15	10/10/1999	5.74	15.85	1.47	15.33	46.37	58.09	40.31	0.00	19.08	29.44	75.12	1.82
ULC #1	11/02/1999	5.48	22.90	0.35	18.18	28.46	32.56	29.90	0.00	18.08	30.30	78.48	3.31
ULC #12	11/02/1999	5.08	21.50	0.02	17.35	86.98	58.26	25.98	0.00	22.15	31.48	48.86	8.32
ULC #24	11/02/1999	5.09	21.90	1.16	23.50	75.06	71.44	35.15	0.00	24.14	34.20	88.23	8.13
LLC #1	11/02/1999	5.78	18.40	1.60	41.64	50.89	66.24	39.04	0.00	25.84	37.73	91.98	1.66
LLC #1	06/22/2000	5.05	12.90	2.15	17.36	35.31	42.02	50.01	0.00	9.81	32.25	69.50	8.91
LLC #10	06/22/2000	4.53	16.40	1.50	15.22	19.86	61.72	41.58	0.00	11.82	56.52	282.46	29.51
ULC #3	09/23/2000	5.54	15.00	-0.43	23.05	73.06	72.47	38.02	0.00	13.52	23.27	28.01	2.88
ULC #5	09/23/2000	5.35	15.00	-0.34	19.37	73.93	58.02	23.87	0.00	9.81	25.67	27.45	4.47
ULC #1	09/26/2000	5.46	14.50	0.58	23.66	51.60	68.23	30.42	0.00	10.99	32.30	56.76	3.47
ULC #15	09/26/2000	5.55	15.60	0.53	37.96	26.22	72.73	28.94	0.00	8.41	32.24	63.15	2.82
LLC #1	09/26/2000	5.67	14.40	1.43	19.25	33.03	50.72	40.07	0.00	12.47	31.56	74.04	2.14
LLC #2	09/26/2000	5.79	16.50	0.71	29.36	74.61	59.65	35.47	0.00	14.31	34.22	109.57	1.62
ULC #1	10/16/2000	5.36	15.30	1.01	21.37	25.31	59.82	35.38	0.00	9.37	32.16	39.37	4.37
ULC #10	10/16/2000	5.41	14.42	0.68	40.86	24.13	59.94	31.41	0.00	6.86	29.35	33.76	3.89
ULC	Maximum	5.55	22.90	1.16	40.86	86.98	72.73	38.02	---	24.14	34.20	88.23	8.32
	Minimum	5.08	14.42	-0.43	17.35	24.13	32.56	23.87	---	6.86	23.27	27.45	2.82
	Median	5.41	15.30	0.53	23.05	51.60	59.94	30.42	---	10.99	31.48	48.86	3.89
	Mean	5.37	17.35	0.40	25.03	51.64	61.50	31.01	---	13.70	30.11	51.56	4.63
	Std Dev	0.18	3.60	0.55	8.50	25.95	12.53	4.58	---	6.28	3.52	21.91	2.12
LLC	Maximum	5.79	18.40	2.20	41.64	74.61	66.24	56.59	---	25.84	56.52	282.46	29.51
	Minimum	4.53	12.90	0.71	15.22	19.86	39.89	35.47	---	9.81	29.44	69.50	1.62
	Median	5.74	15.85	1.50	19.25	40.39	58.09	40.31	---	12.47	33.57	75.12	1.82
	Mean	5.48	15.70	1.58	22.97	42.92	54.05	43.30	---	15.07	36.47	110.69	6.76
	Std Dev	0.50	1.73	0.50	9.60	17.19	10.09	7.34	---	5.57	9.20	77.08	10.38

¹The sample ID number is the bottle number in the autosampler.

Table 4. LeConte Creek base flow analyses.

Sample ID	Sample Date or statistic	pH	Cond., $\mu\text{S/cm}$	ANC	Cl^- , $\mu\text{eq/L}$	NO_3^- , $\mu\text{eq/L}$	SO_4^{2-} , $\mu\text{eq/L}$	Na^+ , $\mu\text{eq/L}$	NH_4^+ , $\mu\text{eq/L}$	K^+ , $\mu\text{eq/L}$	IC Mg^{2+} , $\mu\text{eq/L}$	IC Ca^{2+} , $\mu\text{eq/L}$	H^+ , $\mu\text{eq/L}$
Base flow sampling results													
ULC	08/27/1999	5.96	10.1	18.08	---	---	---	32.09	0.00	11.80	19.98	56.12	1.10
LLC	08/27/1999	6.48	9.5	55.66	---	---	---	44.43	0.00	9.25	20.82	55.63	0.33
ULC	10/01/1999	5.92	14.7	4.55	---	---	---	32.35	0.00	16.36	31.59	84.86	1.20
LLC	10/01/1999	6.42	12.1	28.14	---	---	---	29.61	0.00	13.07	33.43	77.76	0.38
ULC	04/21/1999	5.31	16	3.56	16.11	32.67	64.54	24.21	0.00	7.03	14.76	42.92	4.90
LLC	04/21/1999	6.28	14.6	33.54	18.64	18.58	46.09	23.10	0.00	10.22	23.53	62.50	0.52
ULC	03/24/1999	5.33	17.5	-0.77	17.79	38.73	66.57	20.17	0.00	10.74	24.29	61.26	4.68
LLC	03/24/1999	6.07	15.41	21.16	17.13	25.84	50.80	28.23	0.00	10.56	23.29	54.28	0.85
ULC	Maximum	5.96	17.50	18.08	17.79	38.73	66.57	32.35	0.00	16.36	31.59	84.86	4.90
	Minimum	5.31	10.10	-0.77	16.11	32.67	64.54	20.17	0.00	7.03	14.76	42.92	1.10
	Median	5.63	15.35	4.06	16.95	35.70	65.56	28.15	0.00	11.27	22.13	58.69	2.94
	Mean	5.63	14.58	6.36	16.95	35.70	65.56	27.20	0.00	11.48	22.65	61.29	2.97
	Std Dev	0.36	3.20	8.15	1.19	4.29	1.43	6.02	0.00	3.84	7.12	17.51	2.10
LLC	Maximum	6.48	15.41	55.66	18.64	25.84	50.80	44.43	0.00	13.07	33.43	77.76	0.85
	Minimum	6.07	9.50	21.16	17.13	18.58	46.09	23.10	0.00	9.25	20.82	54.28	0.33
	Median	6.35	13.35	30.84	17.88	22.21	48.45	28.92	0.00	10.39	23.41	59.07	0.45
	Mean	6.31	12.90	34.63	17.88	22.21	48.45	31.34	0.00	10.77	25.26	62.55	0.52
	Std Dev	0.18	2.67	14.91	1.07	5.13	3.33	9.16	0.00	1.63	5.58	10.76	0.23
1997 Summary data													
ULC	Maximum	6.44	20.50	52.28	32.64	45.19	71.37	50.64	2.89	17.74	---	---	---
	Minimum	5.95	10.10	-0.94	13.14	1.62	30.04	22.01	0.00	9.72	---	---	---
	Mean	5.43	16.62	19.25	17.81	24.85	59.41	33.46	0.58	12.17	---	---	---
	Std Dev	0.38	4.28	20.99	8.33	15.79	17.13	10.97	1.29	3.18	---	---	---
LLC	Maximum	6.59	20.70	47.29	22.89	34.21	58.79	38.51	0.00	11.65	---	---	---
	Minimum	6.07	13.36	22.89	11.69	11.46	43.01	27.63	0.00	9.06	---	---	---
	Mean	6.28	16.38	36.19	15.06	19.77	52.26	33.52	0.00	10.24	---	---	---
	Std Dev	0.22	2.69	9.81	4.46	8.85	7.52	4.87	0.00	1.02	---	---	---

Table 5. Comparison of LeConte Creek storm event and base flow analyses.

Sample Site	pH	Cond., $\mu\text{S/cm}$	ANC	Cl^- , $\mu\text{eq/L}$	NO_3^- , $\mu\text{eq/L}$	SO_4^{2-} , $\mu\text{eq/L}$	Na^+ , $\mu\text{eq/L}$	NH_4^+ , $\mu\text{eq/L}$	K^+ , $\mu\text{eq/L}$	IC Mg^{2+} , $\mu\text{eq/L}$	IC Ca^{2+} , $\mu\text{eq/L}$	H^+ , $\mu\text{eq/L}$
Storm event median values minus 1999 base flow median values												
ULC	-0.22	-0.05	-3.52	6.10	15.91	-5.62	2.27	---	-0.28	9.35	-9.83	0.95
LLC	-0.61	2.50	-29.34	1.36	18.18	9.64	11.39	---	2.08	10.16	16.05	1.37
storm event mean values minus 1997 summary mean values												
ULC	-0.06	0.73	-18.85	7.22	26.79	2.09	-2.45	---	1.53	---	---	---
LLC	-0.80	-0.68	-34.61	7.91	23.15	1.79	9.78	---	4.83	---	---	---

Noland Divide

Statistical results of the storm-event samples collected at the NDW sites are summarized in tables 6 and 7. Two sets of storm samples were collected from storm events that occurred in June 1999 and January 2000. Chemical analyses showed similar results for both storm samples at the two NDW streamlets. Some noticeable differences between the data from the two storms exists. For example, nitrate nitrogen concentrations averaged 0.25 milligrams per liter (mg/L) and 0.35 mg/L for the southwest and northeast streamlets, respectively for the June storm; and mean nitrate nitrogen concentrations for the January storm were about 0.65 mg/L for both streamlets.

Some differences in water chemistry also occurred between the two streamlets. The pH values ranged from 5.0 to 5.8 at the northeast streamlet and from 4.7 to 6.0 at the southwest streamlet. Sulfate and dissolved aluminum concentrations were higher in the northeast streamlet. Maximum and median sulfate concentrations were 3 to 4 mg/L in the northeast streamlet and less than 2 mg/L in the southwest streamlet. Dissolved aluminum concentrations were more than twice as high in the northeast streamlet. Maximum dissolved concentrations were about 275 micrograms per liter ($\mu\text{g/L}$) in the northeast streamlet compared to 80 –150 $\mu\text{g/L}$ in the southwest streamlet. The streamlets are only a few feet apart and drain essentially the same area. The difference in the chemistry between these streamlets is not clearly explanatory. These results are generally consistent with long term, weekly sampling of the two streamlets from 1991-1998 which showed statistically significant differences between the two streamlets with the NE streamlet having lower pH, lower ANC, and higher concentrations of chloride, nitrate, sulfate and potassium compared to the SE streamlet. Sulfate showed the greatest difference with the NE having a median sulfate of 40.58 $\mu\text{g/L}$ compared to 28.27 $\mu\text{g/L}$ in the SE streamlet. Although the two streamlets are statistically significantly different, they are probably more similar to each other than to most other streams in the Park although no formal cluster analysis has been performed.

It should also be noted that the median concentrations of total aluminum ranged from 105 to 500 $\mu\text{g/L}$ for the two storms at the two streamlets. One discrete sample collected on the rising limb of the hydrograph during the January 2000 storm in the northeast streamlet had a total aluminum concentration of 1,160 $\mu\text{g/L}$. Moreover, the maximum concentration of total aluminum (3,730 $\mu\text{g/L}$) was measured in the southwest streamlet on the falling limb of the stormflow hydrograph during the June 1999 storm. These concentrations represent aluminum associated with particulate matter in the stream, and dissolved aluminum concentrations associated with these samples does not suggest an increase in bioavailability.

Table 6: Storm samples collected at Noland Divide, June 24, 1999
[N, number of samples; na, not applicable; μ S/cm, microsiemens per liter; μ g/L, micrograms per liter; *, dissolved; mg/L milligrams per liter; <, less than]

Water quality parameter	Maximum	Minimum	Median	Mean	Standard deviation	Maximum	Minimum	Median	Mean	Standard deviation
	Northeast Streamlet (N=6)					Southwest Streamlet (N=6)				
pH (standard units)	5.4	5.0	5.2	na	0.15	5.7	4.7	5.5	na	0.37
Specific conductance (μ S/cm)	22	15	17	18	3.06	13	12	12	12	0.52
Aluminum (μ g/L)	270	180	255	245	53.2	150	70	105	108	33.1
Total Aluminum (μ g/L) (N=2)	470	420	445	445	35.3	3,730	220	na	na	na
Calcium* (mg/L)	1.26	1.08	1.16	1.16	0.06	1.34	0.95	1.0	1.06	0.14
Chloride* (mg/L)	0.23	0.20	0.21	0.21	0.01	0.32	0.22	0.24	0.25	0.04
Fluoride* (mg/L)	<0.1	<0.1	<0.1	na	na	<0.1	<0.1	<0.1	na	na
Magnesium* (mg/L)	0.26	0.24	0.24	0.25	0.01	0.24	0.21	0.22	0.22	0.01
Potassium* (mg/L)	0.50	0.41	0.43	0.44	0.035	0.42	0.26	0.31	0.32	0.06
Silica* (mg/L)	2.8	2.5	2.6	2.63	0.10	3.1	2.7	3.0	2.96	0.17
Sodium* (mg/L)	0.46	0.36	0.37	0.39	0.04	0.48	0.38	0.41	0.42	0.036
Sulfate* (mg/L)	4.0	3.2	3.5	3.52	0.31	1.9	1.8	1.9	1.86	0.05
Ammonia* (mg/L)	0.02	<0.02	<0.02	na	na	0.03	<0.02	<0.02	0.02	na
Nitrate + nitrite* (mg/L)	0.41	0.33	0.34	0.35	0.03	0.27	0.23	0.24	0.25	0.017
Nitrite* (mg/L) (N=2)	<0.01	<0.01	<0.01	na	na	<0.01	<0.01	<0.01	na	na
Total Kjeldahl nitrogen (mg/L) (N=2)	0.23	0.15	na	na	na	2.3	0.19	na	na	na
Phosphorus* (mg/L) (N=2)	<0.05	<0.05	<0.05	na	na	<0.05	<0.05	<0.05	na	na
Orthophosphate* (mg/L) (N=2)	<0.01	<0.01	<0.01	na	na	0.01	0.01	0.01	na	na
Total phosphorus (mg/L) (N=2)	<0.05	<0.05	<0.05	na	na	0.33	<0.05	na	na	na

Table 7: Storm samples collected at Noland Divide, January 9, 2000
[N, number of samples; na, not applicable; $\mu\text{S}/\text{cm}$, microsiemens per liter; $\mu\text{g}/\text{L}$, micrograms per liter, *, dissolved; (mg/L, milligrams per liter; e, estimated value]

Water quality parameter	Maximum	Minimum	Median	Mean	Standard deviation	Maximum	Minimum	Median	Mean	Standard deviation
	Northeast Streamlet (N=6)					Southwest Streamlet (N=3)				
pH (standard units)	5.8	5.2	5.3	na	0.26	6.0	5.6	6.0	na	0.23
Specific conductance ($\mu\text{S}/\text{cm}$)	20	15	19	18	2.23	26	15	16	19	6.1
Aluminum ($\mu\text{g}/\text{L}$)	280	80	255	210	86.7	80	60	70	70	10
Total aluminum ($\mu\text{g}/\text{L}$)	1,160	380	500	612	299	410	240	250	300	95
Calcium* (mg/L)	1.21	1.01	1.15	1.12	0.08	1.15	1.07	1.11	1.11	0.04
Chloride* (mg/L)	0.35	0.32	0.32	0.33	0.01	1.39	0.29	0.30	0.66	0.63
Chromium* ($\mu\text{g}/\text{L}$)	<14	<14	<14	na	na	<14	<14	<14	na	na
Copper* ($\mu\text{g}/\text{L}$)	<10	<10	<10	na	na	6e	<10	<10	na	na
Fluoride* (mg/L)	<0.1	<0.1	<0.1	na	na	<0.1	<0.1	<0.1	na	na
Iron* ($\mu\text{g}/\text{L}$)	17	6	11	11.3	4.5	11	7	10	9.3	2.1
Magnesium* (mg/L)	0.30	0.26	0.29	0.28	0.02	0.33	0.28	0.30	0.30	0.02
Manganese* ($\mu\text{g}/\text{L}$)	<20	<20	<20	na	na	22	<20	<20	na	na
Potassium* (mg/L)	0.45	0.38	0.445	0.43	0.03	2.24	0.37	0.37	0.99	1.08
Silica* (mg/L)	2.8	2.3	2.35	2.43	0.20	3.0	2.6	3.0	2.87	0.23
Sodium* (mg/L)	0.41	0.36	0.375	0.38	0.02	0.74	0.54	0.60	0.63	0.10
Sulfate* (mg/L)	3.2	1.9	3.05	2.77	0.57	1.4	1.3	1.3	1.33	0.06
Zinc* ($\mu\text{g}/\text{L}$)	<20	<20	<20	na	na	22	<20	<20	na	na
Ammonia* (mg/L)	<0.02	<0.02	<0.02	na	na	0.03	<0.02	<0.02	na	na
Nitrate + nitrite* (mg/L)	0.67	0.57	0.645	0.63	0.04	0.68	0.66	0.66	0.67	0.01
Nitrite* (mg/L)	<0.01	<0.01	<0.01	na	na	<0.01	<0.01	<0.01	na	na
Total Kjeldahl nitrogen (mg/L)	0.66	0.10	0.315	0.34	0.24	0.34	0.21	0.23	0.26	0.07
Phosphorus* (mg/L)	<0.05	<0.05	<0.05	na	na	<0.05	<0.05	<0.05	na	na
Orthophosphate* (mg/L)	<0.01	<0.01	<0.01	na	na	<0.01	<0.01	<0.01	na	na
Total phosphorus (mg/L)	0.06	<0.05	<0.05	na	na	0.03e	<0.05	<0.05	na	na

Operational problems

Many lessons were learned from problems encountered in this work and were primarily associated with equipment and the uncertainties of the weather. These problems are listed below:

- The autosamplers were triggered by a stage sensor that operated on water conductivity principles. However, the low conductivity waters of Park caused the sensor not to trigger in some storm events. Also, the trigger was based on a preset stage that would then cause the bottles to fill at set time intervals until all the bottles were filled. A problem occurred due to the drought conditions that dropped the stream stage very low so that a storm event did not raise the stage high enough to trigger sampling. It was also difficult to set the upper and lower sites so that both would trigger during the same storm and at roughly the same time. For example, sometimes the upper site sampler would trigger whereas the lower site would not. A better triggering system would be one based on sensing differentials in stage rather than absolute stage. Also, considerable stage data were lost due to malfunctioning transducers. One of the transducers was sent back to the factory for repair and took several months before it was operating properly.
- Because the samples filled at set time intervals, it was not possible to reliably sample the desired rising limb and peak of the hydrograph due to varying storm lengths. As a result, only partial pH values for a storm were measured. A multiparameter monitor, also called a sonde or probe, is desirable to record and log stage, temperature, conductivity, and pH at 15 minute intervals for at least one month at a time. This would give a better understanding of the extremes and duration of extreme conditions during episodic events.
- Problems were also found in keeping the upper site's battery charged. The site was too shaded to allow a solar cell to fully charge the battery. The problem was solved by closely monitoring the battery's charge and replacing as needed.
- A severe drought occurred during much of the sampling period which limited the size and frequency of the storms that could be sampled.

Conclusions and recommendations

1. pH levels as low as 4.36 were recorded at the upper Le Conte Creek site and 4.44 at Noland Divide were recorded. The Noland Divide pH level is significantly lower than the lowest pH recorded of 4.9 during an October 31- November 5, 1995 storm event. These pH levels are serious concern for aquatic life. The NDW has a wide variety of aquatic biota but it is too small to support fish. The upper Le Conte site is sufficient size to support fish but a viable fish population does not exist in the upper reaches of this stream. Acidification is strongly suspected to be a primary reason for the lack of fish.

The upper and lower Le Conte show an elevation gradient consistent with that observed in the entire Park, i.e., higher elevations have lower pH.

2. The pH dropped 0.06-0.22 at the upper LeConte Creek site and 0.61-0.80 at the lower site LeConte Creek site during storm events when comparisons were made to 1999 base flow samples and 1997 summary data respectively. ANC dropped 3.52-18.85 $\mu\text{eq/L}$ at the upper site and 29.34-34.61 $\mu\text{eq/L}$ at the lower site and essentially eliminated any acid neutralizing capacity in the stream. The lower site unexpectedly showed a greater change in the analytes than the upper site. It was expected that the larger drainage basin at the lower site would attenuate any changes
3. Dissolved aluminum in Noland Divide in several samples exceeded the concern level of 200 $\mu\text{g/L}$. The storm event data compares to a previous storm event study October 31-November 5, 1995 which measured 260 $\mu\text{g/L}$.
4. The observed very low pH levels would prohibit trout populations if they persisted for sufficient time. The aluminum levels greater than 200 $\mu\text{g/L}$ also causes concern. This exploratory storm event research demonstrates the extremes in pH that occur in storm events and the need for increased monitoring and attention to storm events.
5. Several lessons were learned from this research including the desirability of using multiparameter monitors with internal dataloggers (also called sondes and probes) that can be placed in a stream and record and log pH, temperature, conductivity, and stage readings at set intervals, e.g., 15 minutes and be downloaded monthly. Such probes give richer views and more complete understanding of storm events and would be important adjuncts to autosamplers. Autosamplers used should trigger off of differential changes in gauge height and would desirably be refrigerated in cases where samples cannot be retrieved within 24 hours. Preferred technology for operating and triggering the samplers utilizes a pressure transducer that monitors water level, which is connected to a datalogger programmed to control the autosampler. This more sophisticated sampling approach eliminates the guess work, and allows sampling interval to be a function of rate water level change instead of requiring the water level to reach a fixed gauge height. This methodology would provide better coverage over the storm hydrograph and more exact and meaningful sampling. For samplers deployed in remote locations, instrumentation to provide transmissions of real-time streamflow conditions would be helpful to alert field personnel of when samplers had been activated and eliminate unnecessary and unproductive site visits.